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Generation and Reactivity of the Phenyl Cation in Cryogenic Argon Matrices: Monitoring the Reactions with Nitrogen and Carbon Monoxide Directly by IR Spectroscopy

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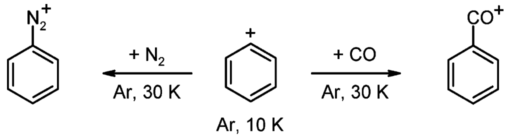
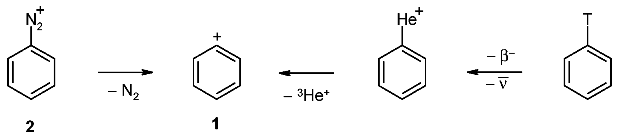


The phenyl cation **1** has been prepared by co-deposition of iodobenzene **6** or bromobenzene **7** with a microwave-induced argon plasma and characterized by IR spectroscopy in cryogenic argon matrices. The cation can clearly be identified by its strongest absorption at 3110 cm^{-1} that is rapidly bleached upon visible light irradiation. This characteristic band is observed neither in the conventional photochemistry of **6** or **7** nor in discharge experiments with alkyl halides or chlorobenzene. The latter finding is in line with energetic considerations. According to density functional theory (DFT) computations, the strongest absorption of **1** is caused by a C−H stretching vibration that involves almost entirely the *ortho*-hydrogens. This is confirmed by isotopic labeling experiments. Co-deposition of halobenzene/N_2 mixtures leads to a decrease of the 3110 cm^{-1} absorption, whereas several new signals are detected in the 2200−2400 cm^{-1} range of the IR spectrum. Annealing of a matrix that contains **1** and 1% N_2 leads to an increase of a broad band at 2260 cm^{-1} that is assigned to the benzenediazonium ion **2**. A sharp signal at 2327 cm^{-1} that had previously been assigned to the N−N stretching vibration of **2** is due to molecular nitrogen. The mechanism that triggers the IR activity of N_2 is not yet understood. Annealing of a matrix that contains **1** and 0.5% CO leads to an increase of a broad band at 2217 cm^{-1} that is considerably stronger than the 2260 cm^{-1} absorption of **2**. This signal is assigned to the C−O stretching vibration of the benzoyl cation **12**, in excellent agreement with previous investigations of **12** in superacidic media. Some consequences of the measured frequencies with regard to bonding in **2** and **12** are discussed.

Introduction

The phenyl cation **1** is of fundamental importance in diazo chemistry[1] and has been the subject of numerous experimental and theoretical studies.[2] According to its high reactivity and low stability, formation of **1** in solution requires precursors with excellent leaving groups such as nitrogen or helium.[1,2] The latter has been introduced into organic compounds by the nuclear decay approach which employs the spontaneous β-decay of covalently bound tritium resulting in transmutation to $^3He^+$.[2,3] Under these conditions, the cations are formed with a rather high excess energy (resulting partly from the energy released upon relaxation of the cation from the geometry of its tritiated precursor). The cations formed in this way can be trapped by various reagents both under gas-phase conditions at different pressures and in solution.[2,3]



Aryl cations bearing appropriate substituents were generated in solution by solvolysis of perflouroalkylsulfonic aryl esters[4] or by solvolytic cyclization of suitable dienynes,[5] but dediazoniation of benzenediazonium ions **2** is the most common and general route to these species. The mechanism of dediazoniation

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(1) Zollinger, H. *Diazo Chemistry*; VCH: Weinheim, 1994; Vol. 1.

(2) *Dicoordinated Carbocations*; Rappoport, Z., Stang, P. J., Eds.; Wiley: Chichester, 1997.

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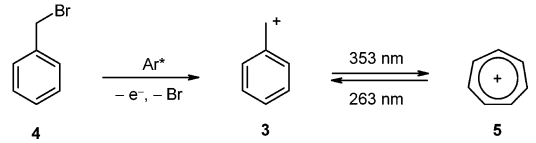
has been subjected to intense research, and even the bare existence of aryl cations in the condensed phase has been debated controversially.[1,2] There are strong indications that this process is considerably more complex in solution than in the gas phase,[1,2,6] where, according to calculations,[7] the extrusion of nitrogen is a strongly endothermic elementary reaction. Attempts to generate and identify (singlet) aryl cations directly by the techniques of laser-flash photolysis (LFP) failed so far owing to their short lifetime ($\leq$0.5 ns)[8] and, probably, their lack of strong UV absorptions above 250 nm.[9] In 1,1,1,3,3,3-hexafluoro-2-propanol, Steenken et al. were able to study several cations by time-resolved spectroscopy, among them the benzyl cation **3**.[10] Starting from various substituted arenediazonium ions, however, no signals of intermediate aryl cations could be detected. Still, these authors demonstrated that aryl cations are formed and can be scavenged by aromatics giving cyclohexadienyl cations.[11] In superacidic media, products indicative of heterolytic dissociation were identified, but aryl cations could not be detected directly.[12] For *para*-amino-substituted aryl cations, which have triplet ground states, it was shown that their lifetime in solution is below 15 ps;[13] these systems are efficiently formed by photoheterolysis of haloanilines in polar or protic solvents, and their chemistry has been investigated in a series of elegant studies by Albini et al.[14] Triplet aryl cations[15] stabilized by several methoxy groups were studied by EPR and UV/vis spectroscopy in LiCl matrices at 77 K.[16]

In contrast to radical cations[17] or small halogenated carbocations (e.g., CCl_3^+),[18] the isolation of unsubstituted (closed-shell) carbocations in cryogenic noble gas matrices has been described in the literature only incidentally. By co-condensation of benzyl bromide **4** with microwave-excited argon, Andrews et al. obtained two novel species with characteristic UV absorptions at 353 and 263 nm that were assigned to the benzyl cation **3** and the tropylium ion **5**, respectively.[19] These isomers can be interconverted photochemically.



The mechanism of energy transfer during co-deposition of organic substrates with excited argon from an open-ended discharge tube has been a matter of debate. Whereas Jacox et al. favored a Penning ionization by collision with argon metastables,[20] Andrews et al. presented compelling evidence for a direct photoionization that takes place on the surface of the forming matrix rather than in the gas phase.[21]

In a preliminary communication, we reported the formation of **1** by co-deposition of iodobenzene **6** or bromobenzene **7** with microwave-excited argon.[22] Matrix-isolated **1** was identified by its strong IR absorption at 3110 cm^{-1}, and this assignment has been confirmed by isotopic labeling experiments. A strong absorption in the same spectral range (3125 cm^{-1}) has more recently been observed by Solca and Dopfer for protonated fluorobenzene in the gas phase, and therefore, this species has

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(4) Early attempts at solvolytic generation of aryl cations were not successful: (a) Streitwieser, A., Jr.; Daffron, A. *Tetrahedron Lett.* **1976**, 1435. (b) Subramanian, L. R.; Hanack, M.; Chang, L. W. K.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099. Following theoretical predictions by Apeloig et al., Sonoda et al. finally achieved the generation and trapping of 2,6-disubstituted aryl cations in fluorinated solvents: (c) Apeloig, Y.; Arad, D. *J. Am. Chem. Soc.* **1985**, *107*, 5285. (d) Himeshima, Y.; Kobayashi, H.; Sonoda, T. *J. Am. Chem. Soc.* **1985**, *107*, 5286.

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(10) (a) McClelland, R. A.; Chan, C.; Cozens, F.; Modro, A.; Steenken, S. *Angew. Chem.* **1991**, *103*, 1389; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1337. See also: (b) McClelland, R. A.; Mathivanan, N.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 4857. (c) McClelland, R. A.; Cozens, F. L.; Li, J.; Steenken, S. *J. Chem. Soc., Perkin Trans. 2* **1996**, 1531.

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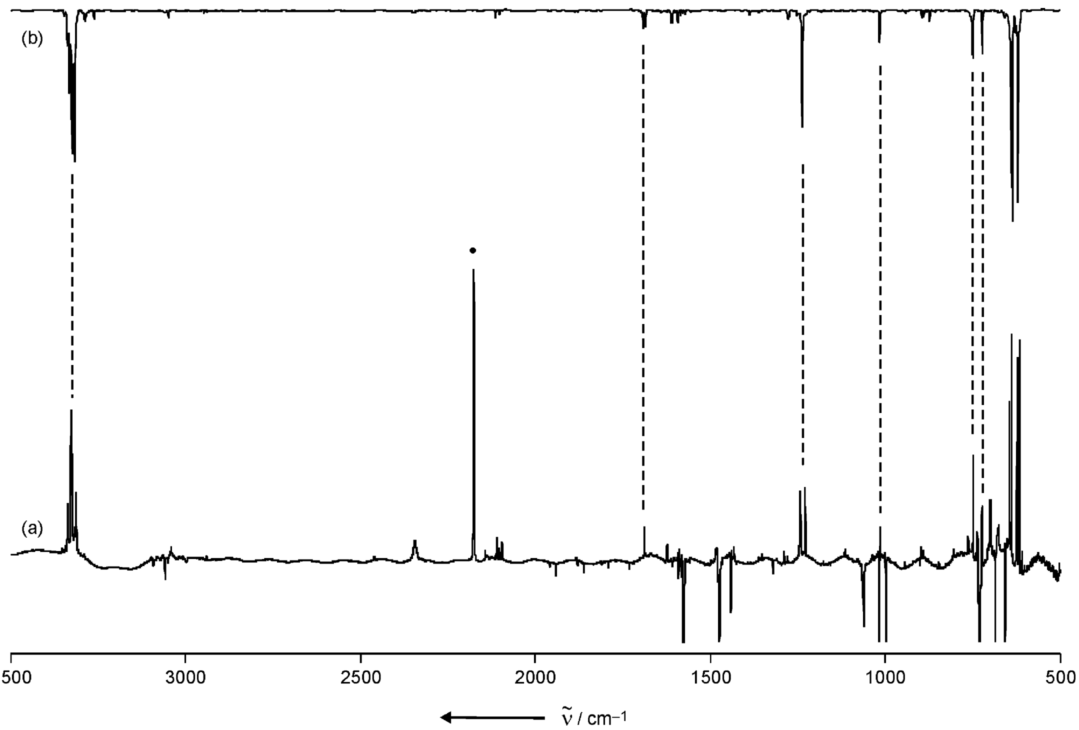
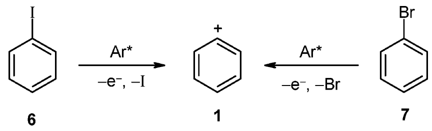


FIGURE 1. Photochemistry of **6** upon long-wavelength irradiation. (a) Difference spectrum; bands pointing upward increase in intensity upon irradiation (λ > 295 nm) of a matrix that contains **6** (Ar, 10 K). The strong absorption at 2175 cm^{-1} (labeled by a dot) is assigned to complexed HI. (b) IR spectrum of (*Z*)-hex-3-ene-1,5-diyne (*Z*)-**9**.

been described as a weakly bound ion−dipole complex of **1** and HF.[23]



We also reported our first attempts to study the intermolecular chemistry of the phenyl cation, particularly, the trapping reaction with molecular nitrogen to give the benzenediazonium ion **2**.[22] One major drawback of our early approach has been the low quality of the matrices that made it impossible to trigger intermolecular reactions in the usual way by annealing the matrices to 30−35 K. Instead, we added successively larger amounts of trapping reagents and followed the changes in the IR spectra in a series of otherwise identical experiments (this procedure has been called "titration"). However, the information gained in this way is necessarily of a rather indirect nature.

In this contribution, we describe the matrix isolation of the phenyl cation in full detail and present additional evidence to support this assignment. Next, we reconsider the reaction of **1** with molecular nitrogen on the basis of improved experimental conditions that make it possible for the first time to follow reactions of an aryl cation directly by IR spectroscopy. Finally, we describe the reaction of **1** with CO under similar conditions.

Results and Discussion

Photochemistry of Iodobenzene 6. The formation of the phenyl radical **8** upon irradiation of **6** with UV light (λ = 254 nm) was observed by EPR spectroscopy already in 1969.[24] The vibrational spectrum of **8** was studied in detail starting from several precursors,[25] and all IR absorptions assigned to the radical are also found in our experiments after 254 nm irradiation of **6** (cf., Figure 2a). In contrast, irradiation of iodobenzene in argon at 10 K with light of wavelength λ > 295 nm gives rise to a different photochemistry (Figure 1).

A strong absorption at 2175 cm^{-1} is assigned to complexed HI; the H−I stretching vibrational frequency is red shifted from monomeric HI (2244 ± 10 cm^{-1} in argon matrices, 2232 cm^{-1} in krypton matrices,[26] and 2227 cm^{-1} in the gas phase[27]) by approximately 60 cm^{-1}, indicating the formation of a complex.

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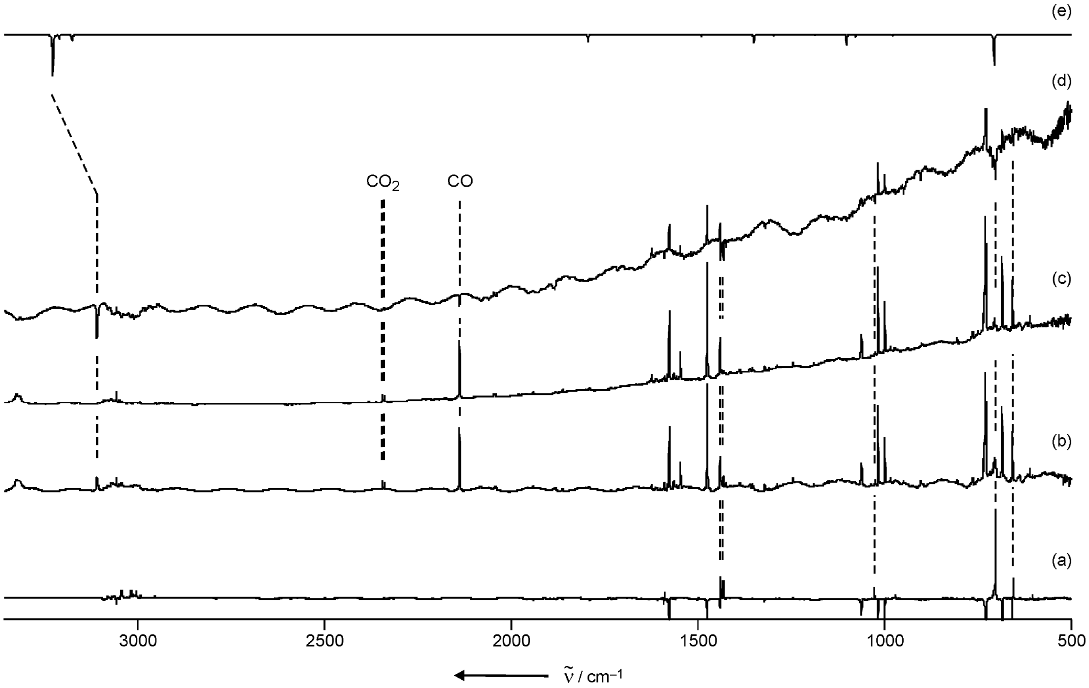
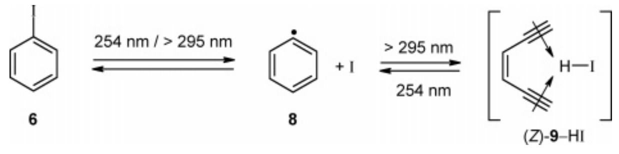


FIGURE 2. (a) Photochemistry of **6** upon short-wavelength irradiation. Difference spectrum; bands of the phenyl radical **8** pointing upward increase in intensity upon irradiation ($\lambda = 254$ nm) of a matrix that contains **6** (Ar, 10 K). (b) IR spectrum of a matrix obtained after co-deposition of **6** with excited argon. (c) The same matrix after irradiation with visible light ($\lambda > 400$ nm). (d) Difference spectrum (c)−(b); bands pointing downward decrease in intensity upon long-wavelength irradiation. (e) Calculated IR spectrum of **1** (B3LYP/aug-cc-pVTZ).

In the system C_2H_2/HI, Abrash and Pimentel observed a complex with an absorption at 2179 cm^{-1}.[28] Additional bands formed upon irradiation of **6** coincide with the IR spectrum of (*Z*)-hex-3-ene-1,5-diyne (*Z*)-**9**, although some of the signals are split because of complexation with HI. No attempts were made to clarify the structure of (*Z*)-**9**-HI, but knowledge of its IR data is important to exclude formation of these byproducts during co-deposition of **6** with excited argon. Formation of (*Z*)-**9**-HI is reversible, and 254 nm irradiation leads back to **8**. Although we cannot strictly rule out a direct ring opening of **6**, there are indications that **8** is formed first and subsequently yields (*Z*)-**9**-HI. Thus, the complex forms more rapidly, if **8**/I is first generated by 254 nm irradiation. Interestingly, no ring-opening reaction is observed under iodine-free conditions, e.g., when **8** is produced from dibenzoylperoxide. In the absence of iodine, the ring opening of **8** requires an activation energy of 67.1 kcal mol^{-1} (UB3LYP/aug-cc-pVTZ) and the resulting hexa-1,3-diene-5-yne-1-yl radical is 61.9 kcal mol^{-1} less stable than the phenyl radical.[29]



Matrix Isolation of the Phenyl Cation 1. The IR spectrum of a matrix obtained after co-deposition of **6** with microwave-excited argon is shown in Figure 2b. Apart from unreacted iodobenzene, the spectrum shows the formation of phenyl radicals as well as some acetylenic byproducts, which give rise to a broad and poorly structured absorption around 3320−3330 cm^{-1}. Another absorption is found at 3110 cm^{-1} and assigned to **1** as proposed previously.[22] Subsequent irradiation of the matrix with light of longer wavelength causes the latter signal and all absorptions of **8** to vanish, whereas the bands of **6** increase in intensity.

Photolability is a characteristic feature of cations with high electron affinity in cryogenic matrices,[18,30] although the photophysical and chemical processes accompanying the photobleaching are not well understood. Increasing the energy and bandwidth of the radiation ($\lambda > 400$ nm; $\lambda > 320$ nm; $\lambda > 305$ nm) causes a faster disappearance of the cation absorption. Most probably, irradiation with UV/vis light induces electron-transfer processes that lead to electroneutralization. In addition, recombinations with nearby iodine atoms occur because of local warming of the matrix upon irradiation. Accordingly, the IR signals of **1** and **8** both decrease, whereas those of **6** increase in intensity during photolysis.

Several points regarding the assignment of the 3110 cm^{-1} peak to **1** are worth mentioning. It is evident from Figure 2 that, apart from the phenyl radical absorptions, there are no additional strong signals in the IR spectrum that decrease in intensity upon long wavelength irradiation. Therefore, the band at 3110 cm^{-1} is caused by a species that has its strongest IR absorption in the high-frequency part of the aromatic C−H stretching regime. This characteristic feature matches exactly our expectations based on DFT calculations for **1** (Figure 2e). A second signal of slightly lower intensity is expected around

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[28] Abrash, S. A.; Pimentel, G. C. *J. Phys. Chem.* **1989**, *93*, 5828.

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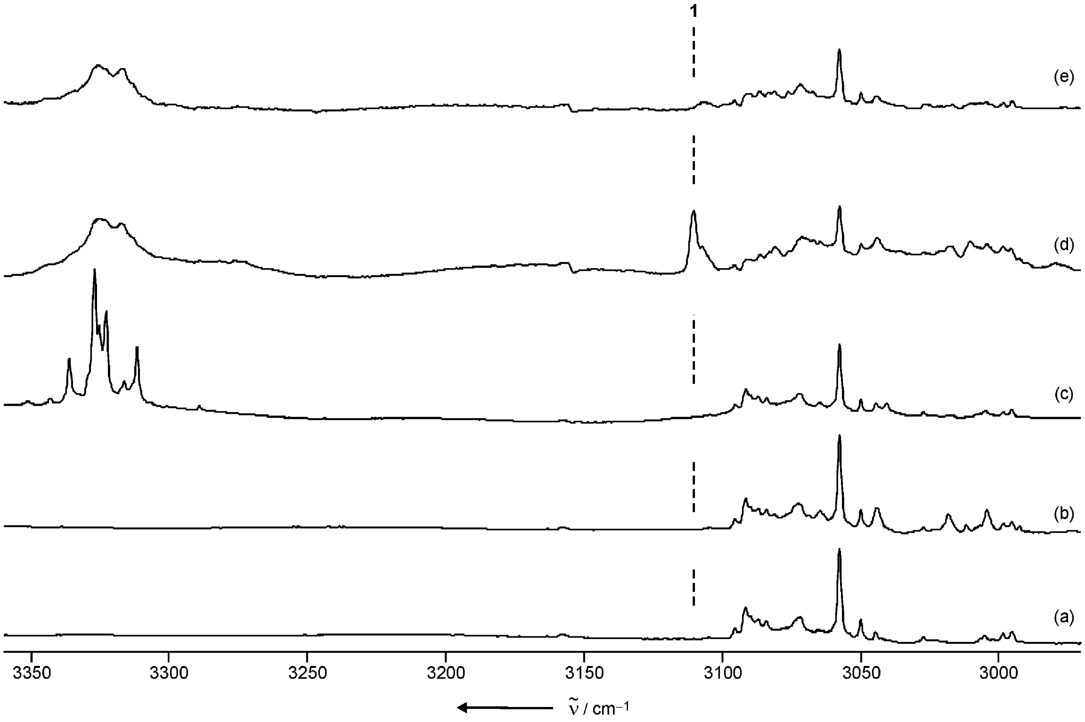


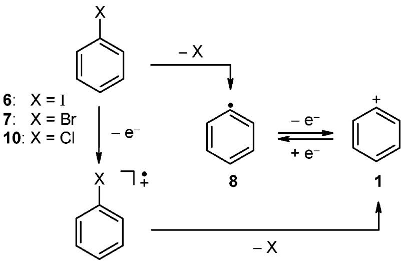
FIGURE 3. (a) IR spectrum of **6**. (b) IR spectrum of a matrix containing **6** after irradiation with $\lambda = 254$ nm. (c) IR spectrum of a matrix containing **6** after irradiation with $\lambda > 295$ nm. (d) IR spectrum of a matrix obtained after co-deposition of **6** with microwave-excited argon. (e) The same matrix after long-wavelength irradiation ($\lambda > 400$ nm).

700 cm^{-1}, very close to the strongest band of **8**. As shown in Figure 2, a photolabile group of absorptions is indeed found in this (less-characteristic) spectral region. Because it is difficult to decide which of these overlapping bands belongs to **1**, the main focus of this work is on the characteristic high-frequency absorption of the phenyl cation.

Another important point relates to the absence of the 3110 cm^{-1} signal in the conventional photochemistry (Figure 3) and in high-temperature experiments with halobenzenes (using different setups for pyrolysis).[31] Thus, formation of this entity relies upon high energies as provided in the discharge experiments (vide infra), whereas the 3110 cm^{-1} absorption is not observed after photochemical or thermal excitation of **6** or **7** with energies below the ionization threshold.

This point can be made more quantitative. The appearance potentials (AP) of **1** from iodobenzene **6**, bromobenzene **7**, or chlorobenzene **10** were determined in various gas-phase studies using different experimental techniques.[32] All values reflect the increasing ionization energy and C−X bond dissociation energy in the series **6** < **7** < **10**. Compared with the gas phase, ionization energies in argon matrices are usually lowered by 0.5−1 eV.[33] As a lower limit of the energy required to produce phenyl cations from halobenzenes on the surface of the forming matrix, we took the mean value of the gas-phase appearance potentials published in the literature (denoted AP$_{\mathrm{mean}}$) and subtracted 1 eV to account for the polarizable environment. These values are listed in Table 1.

TABLE 1. Appearance Potentials (AP) of 1 from 6, 7, and 10[a]



Ph−X	AP$_{\mathrm{min}}$[b]	AP$_{\mathrm{max}}$[c]	AP$_{\mathrm{mean}}$[d]	AP$_{\mathrm{matrix}}$[e]	ref
Ph−Cl (**10**)	11.8	13.2	12.7	>11.7	34
Ph−Br (**7**)	11.7	12.2	11.9	>10.9	35
Ph−I (**6**)	10.6	11.5	11.1	>10.1	36

[a] All energies are given in electronvolts.[32] [b] Lowest values published in the literature. [c] Highest values published in the literature. [d] Mean value of all appearance potentials considered. [e] Estimated lower limit for the AP of **1** on top of the forming argon matrix.

The output of the windowless argon resonance lamp is dominated by the principle argon emission doublet at 104.8 and 106.7 nm (11.6−11.8 eV) under the high-pressure conditions employed in our experiments.[21] Similarly, the excitation energy of the argon metastables is 11.55 and 11.73 eV for the $^3P_2$ and $^3P_0$ states, respectively.[20,37] Regardless of whether the energy transfer occurs via a Penning or a photoionization mechanism,

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(31) This absorption has been detected in neither flash vacuum pyrolysis experiments nor under the conditions of carrier gas pyrolysis (pulsed or conventional). Either **8** or acetylenic fragmentation products of unknown constitution are formed in these experiments.

(32) Data compilation: *NIST Chemistry WebBook, NIST Standard Reference Database Number 69*; Lindstrom, P. J., Mallard, W. G., Eds.; National Institute of Standards and Technology: Gaithersburg, MD, March 2003 (http://webbook.nist.gov).

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TABLE 2. Calculated (B3LYP/aug-cc-pVTZ) and Measured Frequencies of the Strongest Absorptions of Various Phenyl Cation Isotopomers

isotopomer	$\tilde{\nu}_{calcd}$/cm^{-1}	I_{calcd}/km mol^{-1}	$\tilde{\nu}_{exptl}$/cm^{-1}
1	3226	190	3110
4-D$_1$-**1**	3226	190	3110
2,4,6-D$_3$-**1**	2397	98	[a]
D$_5$-**1**	2399	110	[a]
^{13}C$_6$-**1**	3215	189	3098

[a] Not assigned because of the high complexity of the IR spectrum in this spectral range.

the energy available to produce **1** is 11.5−11.8 eV. Comparison with Table 2 indicates that **6** and **7** qualify as precursors for **1**, whereas the appearance potential of **1** from **10** in the gas phase (and very probably also on the matrix surface) exceeds the energy available from the discharge.[38] The IR spectra of matrices obtained after co-deposition of **6**, **7**, and **10** with excited argon are given in Figure 4. In agreement with the energetic considerations outlined above, the photolabile absorption at 3110 cm^{-1} is found with iodo- and bromobenzene but is absent from the IR spectrum when **10** is used as a precursor instead.

Assignment of the 3110 cm^{-1} band to **1** is further supported by isotopic labeling. The displacement vector of the normal mode associated with this absorption is shown in Figure 5. The vibration involves mainly the *ortho*-hydrogens with small contributions from a C$_{meta}$−H stretching mode, whereas the C$_{para}$−H moiety does not participate at all.

Accordingly, co-deposition of 4-D$_1$-**7** with excited argon yields 4-D$_1$-**1** without changing the frequency and intensity of the 3110 cm^{-1} feature (Figure 6, Table 2). In contrast, no signal is observed in this spectral range when 2,4,6-D$_3$-**1** is generated from the corresponding 2,4,6-D$_3$-**7** isotopomer. The C−D stretching vibration of 2,4,6-D$_3$-**1** as well as that of the fully deuterated cation D$_5$-**1** is of much lower intensity and could not be identified with certainty because many overlapping bands occur in the 2220−2320 cm^{-1} range of the IR spectrum in experiments with D$_5$-**6**, D$_5$-**7**, and 2,4,6-D$_3$-**7**. In ^{13}C$_6$-**1** (from ^{13}C$_6$-**7**), the photolabile absorption is found at 3098 cm^{-1}. The measured red shift of 11.8 cm^{-1} agrees favorably with the shift of 11.0 cm^{-1} calculated at the B3LYP/aug-cc-pVTZ level of theory.

The high frequency of the C$_{ortho}$−H stretching vibration may seem counterintuitive at first glance. The small CCC angle at the *ortho*-carbon atoms implies a high degree of *s*-character for the σ(C(sp^2)−H) bonding orbital. In addition, the C$_{ortho}$−H bond is strongly polarized (atomic NPA charges[39] of **1** are also given in Figure 5). Both effects outweigh the release of electron density from the C−H bonding region by σ(C$_{ortho}$−H) → n^*(C$_{ipso}$) hyperconjugation. Electrostatic arguments are also employed in the next section to rationalize the N−N and C−O stretching vibrational frequencies in the benzenediazonium ion **2**, the borabenzene−nitrogen adduct **11**, and the benzoyl cation **12**.

Reaction with N$_2$. Because **1** is accessible in cryogenic argon matrices only in low concentrations, the investigation of its intermolecular chemistry is restricted to unreactive (selective) reactants that give rise to very strong and characteristic IR chromophores. The reaction with dinitrogen is a barrierless process (Figure 7),[7] which is exothermic by 28.3 kcal mol^{-1} (B3LYP). The IR intensity of the N−N stretching vibration of **2** amounts to 247 km mol^{-1} (Table 3) so that the benzenediazonium ion should be easily detectable by IR spectroscopy, even if only modest concentrations can be achieved by the intermolecular reaction of **1** with N$_2$.

Our early approach to the trapping chemistry of **1** employed the addition of successively larger amounts of nitrogen under otherwise identical conditions. This titration procedure was necessitated by the observation that matrices obtained by deposition of microwave-excited argon are of rather low quality, so that subsequent annealing led to strong baseline shifts in the IR spectra. The titration with N$_2$ (cf., ref 22) gave rise to an intense and sharp signal at 2327 cm^{-1} and a broad and weaker absorption at 2260 cm^{-1}. On the basis of the high intensity and the good agreement between calculated and measured shifts upon substitution of ^{14}N$_2$ by ^{15}N$_2$, we assigned the former band to the N−N stretching vibration of **2**.[22] However, a signal with the same frequency could be observed in subsequent experiments with alkyl halide/N$_2$ mixtures. The carrier of this trace is, therefore, not the benzenediazonium ion **2**, but polarized dinitrogen. The mechanism that triggers the IR activity of N$_2$ is not clear, but activation under discharge conditions or in the presence of suitable impurities is not without precedence.[40,41] In nitrogen matrices, a very weak absorption at 2328−2329 cm^{-1} has been observed in discharge experiments with CO$_2$/N$_2$ mixtures.[41] In the gas phase, the N$_2$ stretching vibration has been detected by Raman spectroscopy at 2330 cm^{-1}.[42]

The quality of cryogenic argon matrices produced by the slow spray-on technique is often improved by maintaining the temperature of the spectroscopic window during condensation between 25 and 30 K and reducing it afterward (down to 3−10 K) for photochemical investigations.[43] On the other hand, a higher temperature (lower viscosity) clearly supports aggregation or intermolecular reactions. To improve the quality of the matrices, we studied the co-deposition of **6**/N$_2$/Ar mixtures (ca. 1:10:400) with excited argon (the final N$_2$ concentration is approximately 1%) at various temperatures of the spectroscopic window during deposition (between 3 and 25 K) and followed the intensity changes of the 3110 cm^{-1} absorption. For temperatures above 22 K, the yield of **1** decreases rapidly, as expected for a "hyper-reactive"[16b] species. In the temperature range 17−20 K, the intensity of the 3110 cm^{-1} signal is only modestly reduced compared with the lowest-temperature experiments. It turned out, however, that the matrices obtained under these conditions can be subsequently annealed without significant baseline shifts (Figure 8).

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(35) Lowest AP: (a) Rosenstock, H. M.; Stockbauer, R.; Parr, A. C. *J. Chem. Phys.* **1980**, *73*, 773. Highest AP: (b) Burgers, P. C.; Holmes, J. L. *Org. Mass Spectrom.* **1982**, *17*, 123. See ref 32 for details.

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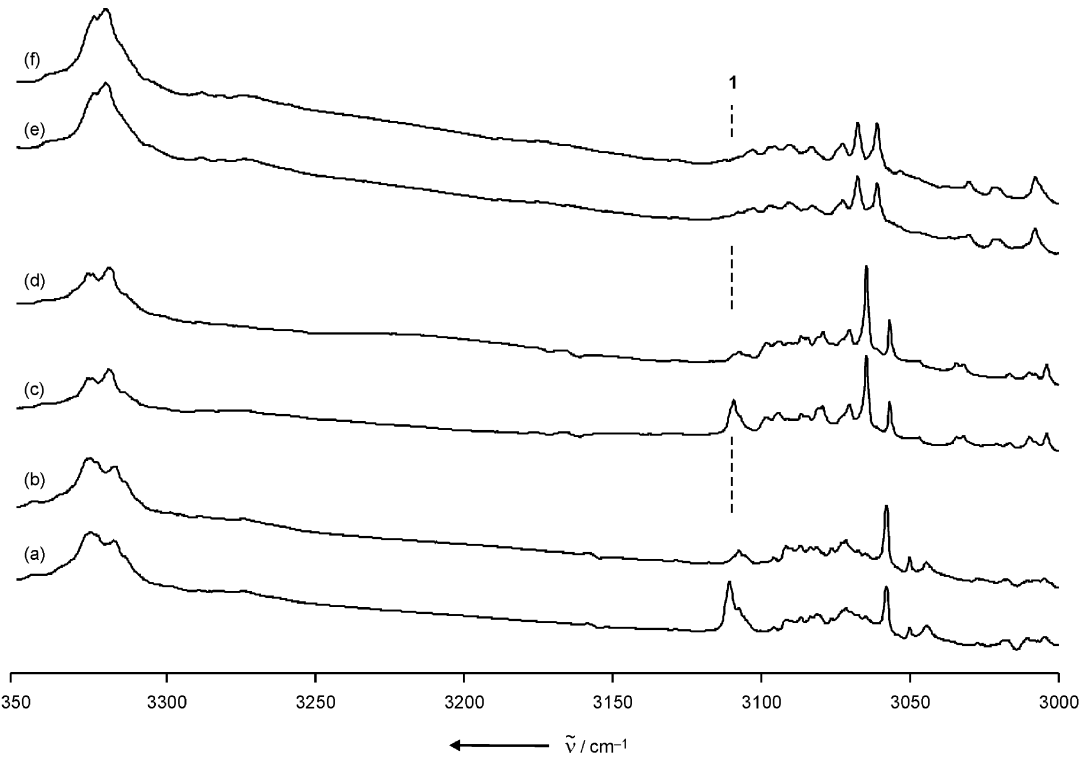

FIGURE 4. (a) IR spectrum of a matrix obtained after co-deposition of **6** with excited argon. (b) The same matrix after long-wavelength irradiation (λ > 400 nm). (c) IR spectrum of a matrix obtained after co-deposition of **7** with excited argon. (d) The same matrix after long-wavelength irradiation. (e) IR spectrum of a matrix obtained after co-deposition of **10** with excited argon. (f) The same matrix after long-wavelength irradiation.

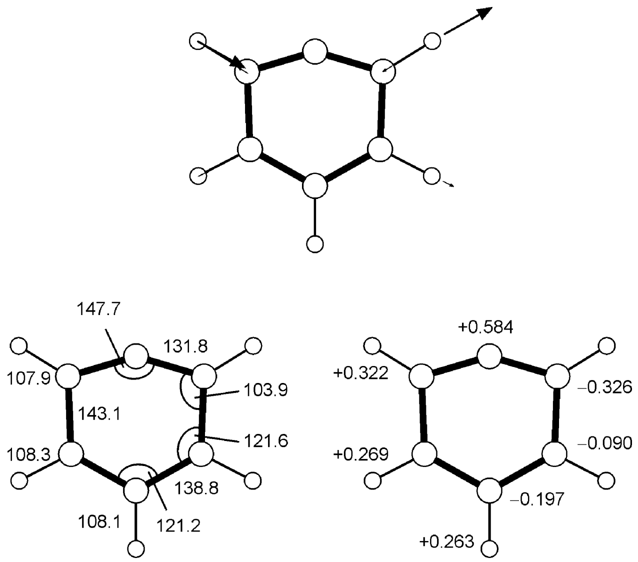

FIGURE 5. Structure of the phenyl cation and displacement vector of the b_2 symmetric C−H stretching vibration that gives rise to the strongest IR absorption of **1** (B3LYP/aug-cc-pVTZ). NPA charges (B3LYP/cc-pVTZ//aug-cc-pVTZ) are given for comparison.

The absorption at 2327 cm^{-1} is of considerably lower intensity than in our earlier titration experiments at 10 K, in line with the lower nitrogen concentration employed here.[22] On annealing to 30 K, the 3110 cm^{-1} signal vanishes rapidly (Figure 8b), whereas a broader absorption at 2260 cm^{-1} increases slightly in intensity. This signal is not affected by H/D exchange of the phenyl hydrogens, in agreement with B3LYP calculations for **2**. Furthermore, it is absent in the CH_3I/N_2 system and in all experiments without nitrogen addition. In experiments with $^{15}N_2$, a broad feature is observed at 2180 cm^{-1} that may tentatively be assigned to $^{15}N_2$-**2**. The measured red shift of 80 cm^{-1} agrees well with the shift of 79 cm^{-1} calculated at the B3LYP level. However, this absorption overlaps with a side product that is also formed in experiments without nitrogen addition. Thus, to identify the N−N stretching frequency of $^{15}N_2$-**2** with certainty, additional improvements of the experimental technique are necessary to achieve significantly higher concentrations of the diazonium ion.

Numerous investigations have been devoted to the structures[44] and the vibrational spectra (measured as Nujol mulls) of benzenediazonium salts.[1,45] Depending on the counterion, N−N stretching frequencies between 2250 and 2310 cm^{-1} have been reported. Attempts to combine these data with information from X-ray structure determinations[44] to clarify the influence of anions and to derive the intrinsic properties (bond strength, charge distribution) of **2** have been disputed controversially.[44a] According to the dative bond model of diazonium ions developed by Glaser et al. on the basis of topological electron density analysis,[46] **2** is best described in terms of a phenyl cation and a polarized N_2 moiety that, as a whole, remains essentially uncharged. The σ-dative charge transfer from N_2 to **1** is largely compensated by $\pi(C_6H_5) \rightarrow \pi^*(N_2)$ back-bonding. Whereas the

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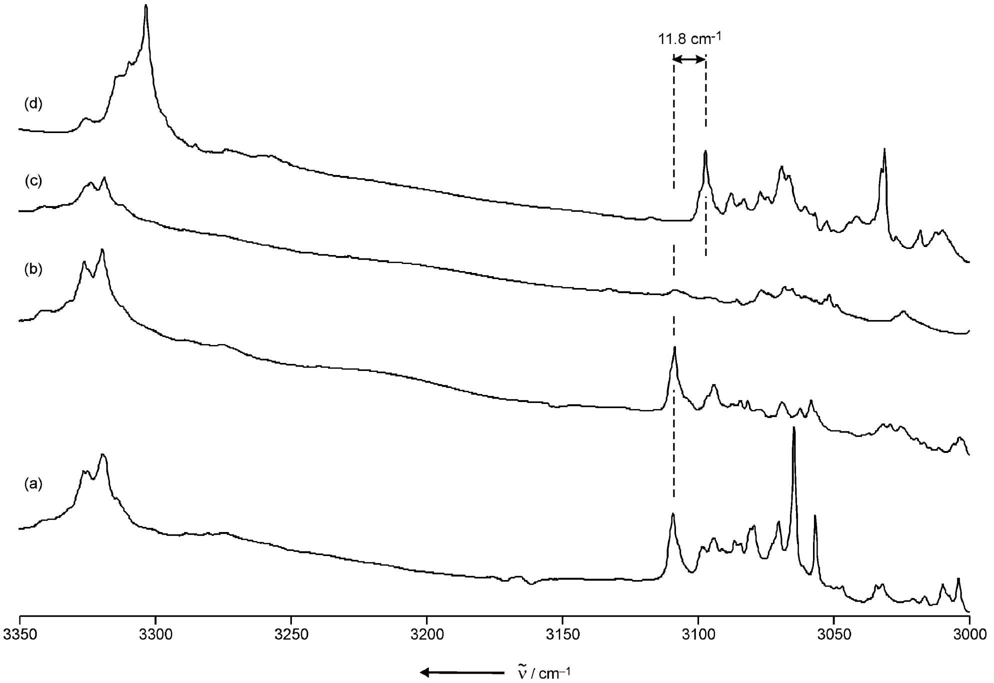


FIGURE 6. IR spectrum of a matrix obtained after co-deposition of different isotopomers of **7** with excited argon. (a) **7**. (b) 4-D_1-**7**. (c) 2,4,6-D_3-**7**. (d) $^{13}C_6$-**7**.

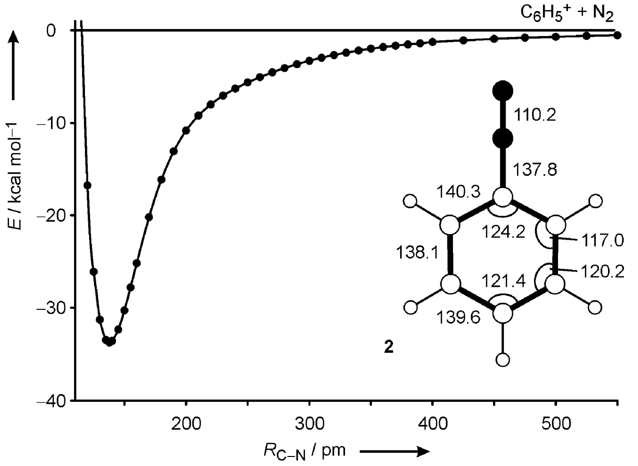


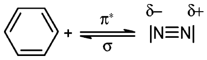
FIGURE 7. Energy as a function of the C−N distance in **2**. For each point, the C−N distance was constrained to a certain value and all other coordinates were optimized at the B3LYP/aug-cc-pVTZ level.

TABLE 3. N−N Stretching Vibrational Frequencies and Bond Lengths of the Methanediazonium and Benzenediazonium Ions and Their Isoelectronic but Neutral Boron Counterparts

system	R_{N-N}/pm[a]	$\tilde{\nu}_{calcd}$/cm^{-1} [a]	I/km mol^{-1} [a]	$\tilde{\nu}_{exptl}$/cm^{-1}
$CH_3-N_2^+$	109.08	2464	1	
N_2	109.12	2447	0	2327[b]
BH_3-N_2	109.49	2384	88	
$C_6H_5-N_2^+$ (**2**)	110.17	2342	247	2260[b]
$C_5H_5B-N_2$ (**11**)	110.70	2269	838	2198[c]

[a] B3LYP/aug-cc-pVTZ. [b] Ar, 10 K; this work. [c] Nitrogen matrix; ref 47.

latter weakens the N−N bond, the internal polarization of the N_2 group (with N_α negatively polarized and N_β positively polarized) leads to additional Coulomb interaction which strengthens the bond.



The data given in Table 4 support this point of view. The N−N bond in **2** is stronger than in the isoelectronic but neutral borabenzene−N_2 adduct **11**, prepared in a nitrogen matrix by Maier and co-workers.[47] On the other hand, it is weaker than in the methanediazonium ion because CH_3^+ is strongly polarizing, whereas back-bonding effects are (virtually) absent. The N−N stretching vibration in the latter ion is calculated to be even blue shifted from dinitrogen.

Reaction with CO. The benzoyl cation **12** has been studied spectroscopically in weakly coordinating media, and X-ray structures of various salts are known.[48] The degree of complexation and intermolecular perturbation by counterions is difficult to assess, however, and spectroscopic data of free acylium ions are, therefore, highly desirable. According to DFT calculations, the addition of **1** to the carbon atom of carbon monoxide is exothermic by 64.8 kcal mol^{-1}, whereas addition to the oxygen atom is considerably less favorable (Figure 9). The C−O stretching frequency of **12** is predicted to be blue shifted from CO by 79 cm^{-1} (Table 4), and the calculated intensity (930 km mol^{-1}) is approximately 4 times larger than the strongest absorption of **2**.

The blue shift of the C−O stretching mode hints again at electrostatic effects. The strengthening of the C−O bond in HCO^+ and the weakening in COH^+ have been investigated in

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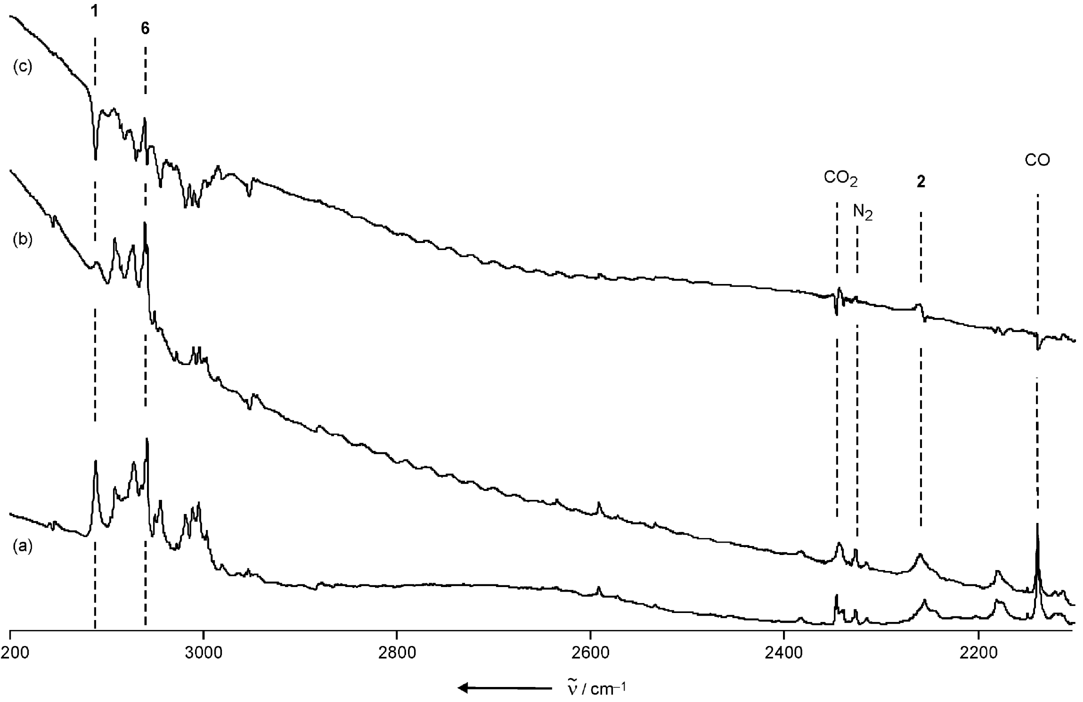

FIGURE 8. (a) IR spectrum of a matrix obtained by co-deposition of a mixture of **6**/N_2/Ar (ca. 1:10:500) with excited argon. (b) The same matrix after short annealing at 30 K. (c) Difference spectrum; bands of **2** and **6** pointing upward increase in intensity upon annealing.

TABLE 4. C−O Stretching Vibrational Frequencies and Bond Lengths of Acylium Ions and Their Isoelectronic but Neutral Boron Counterparts

system	R_{C-O}/pm ^{a}	$\tilde{\nu}_{calcd}$/cm$^{-1\,a}$	I/km mol$^{-1\,a}$	$\tilde{\nu}_{exptl}$/cm^{-1}
CH_3−CO^+	111.31	2373	226	
C_6H_5−CO^+ (**12**)	112.61	2287	930	2217^b
CO	112.58	2208	80	2138^b
BH_3−CO	112.95	2206	494	
C_5H_5B−CO	113.82	2148	1408	
C_6H_5−OC^+ (**13**)	114.76	2015	248	

^{a} B3LYP/aug-cc-pVTZ. ^{b} Ar, 10 K; this work.

some detail.[49] Upon protonation, the C−O localized molecular orbitals become less polarized in the former but more polarized in the latter. It was argued that the more even distribution of π electrons between C and O leads to stronger covalent bonding in HCO^+, whereas the covalent character is lowered in COH^+.[49] This interpretation differs considerably from the bonding model in the diazonium ions mentioned above, according to which internal polarization results in a strengthening of the N−N bond. A more detailed comparison of diazonium and acylium ions seems to be necessary to fully understand the complex interplay of factors determining the variations in N−N and C−O bond strengths in these systems. The availability of experimental data for essentially unperturbed ions should facilitate these investigations.

Co-deposition of **6**/CO/Ar or **7**/CO/Ar mixtures (1:5:500) with excited argon gives rise to a broad absorption at 2217 cm^{-1} (Figure 10) that is more intense than the 2260 cm^{-1} absorption of **2** and further increases on short annealing to 30 K, whereas the 3110 cm^{-1} signal of **1** decreases concomitantly. The frequency (and also the higher intensity compared with **2**, assuming similar concentrations of trapping products) is in excellent agreement with the DFT calculations for **12** outlined above.

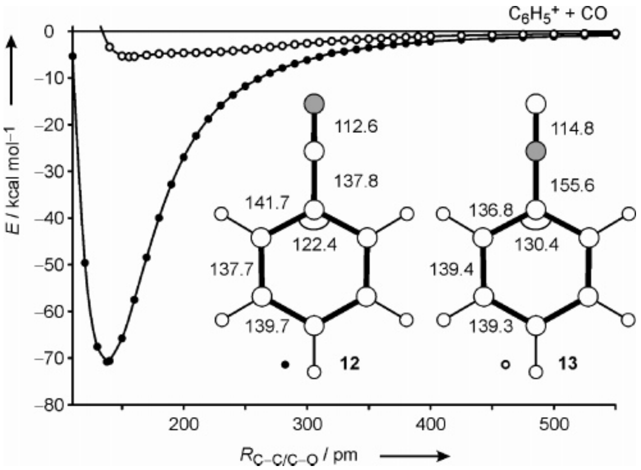

FIGURE 9. Energy as a function of the C−CO distance in **12** and the C−OC distance in **13**. For each point, the bond length was constrained to a certain value and all other coordinates were optimized at the B3LYP/aug-cc-pVTZ level.

The measured C−O stretching frequency agrees well with previous IR measurements under Lewis acidic conditions. In the system C_6H_5COF/SbF_5, a very strong vibration at 2212 cm^{-1} has been attributed to **12**, and a similar frequency (2215 cm^{-1}) has been measured in the system $C_6H_5COCl/SbCl_5$.[48a] In a recent gas-phase study, Oomens et al. assigned a very broad absorption at 2196 cm^{-1} with a strong tailing toward higher frequencies to the C−O stretching mode of **12**.[48c] Although it has been noted that this range is characteristic of acylium ion formation,[48b] it

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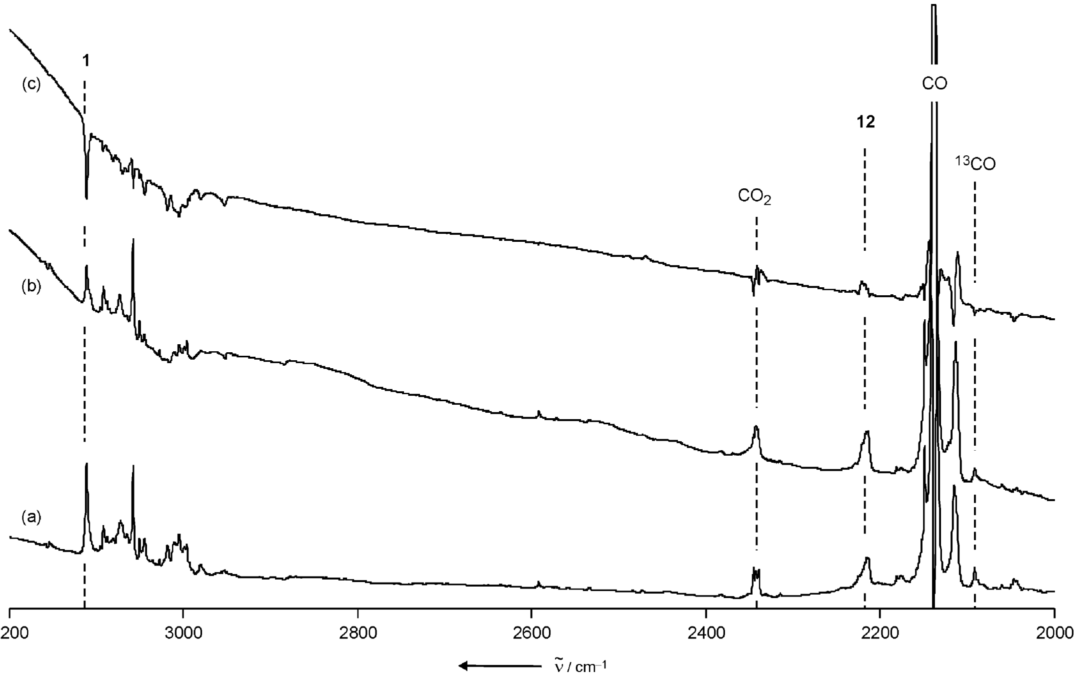

FIGURE 10. (a) IR spectrum of a matrix obtained by co-deposition of a mixture of **6**/CO/Ar (ca. 1:5:500) with excited argon. (b) The same matrix after short annealing at 30 K. (c) Difference spectrum; the absorption of **12** pointing upward increases in intensity upon annealing.

is important to remark that some smaller signals around the same frequency are also observed in discharge experiments with CH_3I/CO mixtures. Although we consider the assignment of the 2217 cm^{-1} trace to **12** likely, all structural assignments based on a single IR absorption (especially in potentially very complex mixtures of charged and neutral compounds) necessarily bear a high risk of misinterpretation and should be considered with some caution. The investigation of more complex chemical reactions of hyper-reactive carbocations in noble-gas matrices clearly requires significant improvements of the experimental techniques available today. Attempts in this direction are currently in progress in our laboratory.

Conclusions

The phenyl cation is accessible in cryogenic argon matrices by co-deposition of **6** and **7** with a microwave-induced argon plasma. It is readily identified by its strong IR absorption at 3110 cm^{-1}, and various arguments in support of this assignment are discussed. A careful optimization of all experimental parameters is essential to study intermolecular reactions of **1** directly by IR spectroscopy. Because only small amounts of the title cation can be isolated, the approach outlined here is applicable only to selective reactants such as nitrogen or carbon monoxide that give rise to very strong and characteristic features in the IR spectrum. The N−N and C−O stretching frequencies of the benzenediazonium ion **2** and the benzoyl cation **12** have been detected at 2260 and 2217 cm^{-1}, respectively. The availability of precise stretching frequencies of essentially free diazonium and acylium ions should be helpful to understand the complex interplay of factors contributing to variations in bond strengths in these compounds and to assess the degree of perturbation by counterions in the corresponding salts.

Experimental Section

Experimental Methods. 4-D$_1$-bromobenzene 4-D$_1$-**7** was prepared from 1,4-dibromobenzene,[50] and 2,4,6-D$_3$-bromobenzene 2,4,6-D$_3$-**7** was prepared from aniline[50b,51] by procedures described in the literature. Matrix isolation experiments were performed by standard techniques[43] with closed cycle helium cryostats. Infrared spectra were recorded with Bruker IFS 66 and Equinox 55 FTIR spectrometers with a standard resolution of 0.5 cm^{-1} using a N_2(l) cooled MCT detector in the range 400−4000 cm^{-1}. For irradiation at 254 nm, a low-pressure mercury arc lamp was employed. Broadband irradiation was carried out with Osram HBO 500 W/2 or Ushio USH-508SA mercury high-pressure arc lamps in Oriel housings equipped with quartz optics and dichroic mirrors in combination with Schott cutoff filters. IR irradiation from the lamps was absorbed by a 10-cm path of water. The discharge tube (quartz; 20 cm; 1 cm o. d.) for argon excitation was opened to the high-vacuum side by a 2 mm orifice and arranged normal to the spectroscopic window (CsI). A Sairem GMP 03 KE (300 W, 245 MHz) magnetron diathermy unit operated at 75 W in combination with an air-cooled cavity, placed near the middle of the tube, was used to excite the discharge. Argon was flowed through the quartz tube at rates necessary to maximize the glow intensity and mixed with the sample/argon mixtures from a second spray-on line ca. 4 cm in front of the cold window.

Computational Methods. Geometries of all species were fully optimized at the B3LYP level,[52] and analytic second derivatives were calculated to characterize stationary points as minima or transition states. Tight convergence criteria for gradients (with maximum residual forces on nuclei below 0.000015 au) and a full (99, 590) integration grid, having 99 radial shells per atom and

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590 angular points per shell, have been used throughout to obtain accurate values for geometries and low-frequency vibrational modes. If not mentioned otherwise, Dunning's aug-cc-pVTZ basis set has been used.[53] All energies reported in the text are zero-point corrected. For NBO analysis, diffuse functions were omitted (B3LYP/cc-pVTZ//aug-cc-pVTZ). All calculations were carried out with Gaussian 98.[54]

Acknowledgment. Financial support by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged.

Supporting Information Available: Cartesian coordinates, vibrational frequencies, and absolute energies of calculated structures are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

JO0603678

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